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ON MICROWAVE (ROTATIONAL) SPECTROSCOPY

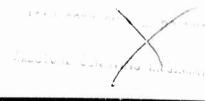
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James E. Wollrab

August 1965







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A BIBLIOGRAPHY

ON MICROWAVE (ROTATIONAL) SPECTROSCOPY

by

James E. Wollrab

Aerodynamics Branch Advanced Systems Laboratory Directorate of Research and Development U.S. Army Missile Command Redstone Arsenal, Alabama

ABSTRACT

The references listed in this bibliography include a majority of the important papers and books that are related to the development of microwave spectroscopy. General references relating to the basic concepts of rotational and, in a limited way, vibrational spectroscopy are also included. Titles of dissertations, reports which have not been published in the open literature, and abstracts of papers presented at spectroscopy symposia generally are not given. Rather than a pure chronological listing, the references have been placed under specific topic headings whenever possible. A chronological order under these headings is maintained. Since a unique classification of each article is impossible, references which do not fall directly under one of the specific topics are listed in Section XII.

Several other bibliographies are available. Townes and Schawlow compiled a complete listing up through 1954. In addition, Favero³⁵ has compiled a bibliography covering 1954 through 1962, and Starck³⁹ has completed one for 1945 through 1962. However, the latter two are not as generally available as might be desired. (See Section I.)

This bibliography includes a majority of the references concerning microwave spectroscopy through 1964, and a number of references from early 1965. Titles are listed to enable a better preliminary assessment of the articles. The listing is a print from IBM cards and a special notation is required in some instances. Atomic weights are given in parentheses following the atomic symbol, e.g., N(14) for N¹⁴. All letters are in the upper case, e.g., L-TYPE DOUBLING is written for *l*-type doubling. Numerical subscripts are written on the same level as the atomic symbol, e.g., H2S is written for H₂S.

Preceding some of the reference lists are very brief resumes. These are not intented to serve as reviews of each area but merely to point out some of the more important or recent progress in each area.

CONTENTS

	Page
Section I. GENERAL AND REVIEW ARTICLES	1
Section II. INSTRUMENTATION	5
Section III. LINE SHAPE AND LINE BROADENING	15
Section IV. THE RIGID ROTOR	19
Section V(a). GENERAL VIBRATION-ROTATION INTERACTION	25
Section V(b). CENTRIFUGAL DISTORTION	27
Section V(c). CORIOLIS COUPLING	29
Section V(d). L-TYPE DOUBLING	30
Section VI. MOLECULAR STRUCTURE	33
Section VII. QUADRUPOLE COUPLING	37
Section VIII. HINDERED INTERNAL ROTATION	45
Section IX. INVERSION	55
Section X. STARK EFFECT	61
Section XI. FLECTRONIC AND MAGNETIC EFFECTS (ZEEMAN EFFECT)	65
Section XII. GENERAL MICROWAVE PAPERS	71

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Section II. INSTRUMENTATION

A majority of microwave studies have been carried out using the conventional square-wave Stark-modulated microwave spectrometer^{5, 11, 21, 24, 112} employing phase-sensitive detection and a reflex klystron source. Measurements have been extended from X-band up into the millimeter wave region through the use of harmonic generators and the development of high frequency tubes. 45, 46, 62, 63, 89, 93, 128 Sensitivity and resolution have been improved by frequency stabilization of the source.

The demonstration of maser principles led to their use in the study of rotational spectra. Very narrow line widths have been achieved with beam-maser spectrometers 100,113 allowing the observation of hyperfine splittings which are too small to be resolved on a conventional spectrometer. Maser action has also been used to identify weak transitions when they have levels in common with stronger lines whose quantum numbers are known. 94, 106

Although Stark effect spectrometers predominate, Zeeman effect studies ^{32, 33, 107} have been accomplished using a variety of cell designs. Other specialized microwave spectrometers include cells with "flow-through" systems for the study of short-lived free radicals, parallel plate absorption cells for precision dipole moment measurements, ⁷² radio frequency and microwave molecular beam devices, ^{73, 116, 119} and high-temperature cells. ^{31, 48, 51} Relative and absolute absorption intensities, as well as line width measurements, also require specialized system design. ^{85, 102, 111, 141} Millimeter wave transitions are being investigated as a possible source for a millimeter frequency standard. ^{122-126, 132-135}

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 FIRST-ORDER LONDON DISPERSION FORCES AND MICROWAVE SPECTRAL LINEWIDTH

Section IV. THE RIGID ROTOR

Calculation and characterization of the energy levels and wave functions of the rigid rotor immediately followed the introduction of the new quantum theory. $^{1-5}$ Application of group theory to the problem considerably simplifies the computational difficulties presented by the asymmetric rotor whose energy levels cannot be expressed in a closed form except for low J values. Since the formulation of the reduced energy $E(\kappa)$, 8,9 the original tabulations of this parameter, 9,17,22 have been extended to high J values for smaller intervals of κ through the use of high-speed digital computers. $^{19,47,49-53}$ Approximate methods were also developed, 11,12 particularly for near symmetric top molecules. $^{25-27,41,42}$ Considerable attention has also been given to the calculation of theoretical line intensities. 10,18,32

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Section VI. MOLECULAR STRUCTURE

Most microwave structure determinations have been carried out using the general isotopic substitution formulas in terms of the equilibrium moments of inertia developed by Kraitchman. The r_s and r_o structures have been compared and discussed regarding the equilibrium structure, and a double substitution technique has been devised to treat small coordinate. The effects of molecular vibrations on the molecular structure and, in particular, on the inertia defect 37, 34, 37, 39, 42 determined from microwave data have received considerable attention.

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Section VII. QUADRUPOLE COUPLING

Nuclear quadrupole interactions can perturb the rotational spectrum of a molecule which contains one or more nuclei with nonspherical nuclear charge distributions. These effects have been studied in linear, symmetric, and asymmetric top molecules 19, 21 to provide information concerning the electric field gradient at the quadrupole nucleus. Second-order effects can become prominent when the quadrupole interaction is sizable or when an appropriate near degeneracy is present. 100, 102, 103 In the case of an asymmetric rotor, the secondorder interaction may lead to an evaluation of an off-diagonal coupling constant Xii. Intensities of the hyperfine components have been adopted directly from atomic spectra. 2,3 Bersohn³⁷ and Misushima and Ito48 have treated the case of three quadrupole nuclei in a symmetric rotor. Work has also been done on asymmetric rotors with two quadrupole nuclei. 104-106, 109, 112 As experimental sensitivity is improved, coupling in excited vibrational states may be studied. 86,88 Interactions with an external electric field are referenced in Section X.

Excellent reviews on the subject have been written by Das and Hahn⁹⁷ and O'Konski. ¹⁰⁷

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Section VIII. HINDERED INTERNAL ROTATION

Studies of internal rotation by microwave spectroscopy have been favored by the relative barrier heights hindering internal rotation in methyl groups and the relatively low vibrational frequencies associated with these torsional motions. Most of the barriers for CH₃-X type molecules, where X represents the frame of the molecule, fall in the region from 1-4 kilocalories which allows splitting of rotational transitions by rotation-internal rotation interactions to be observed either in the ground vibrational state or in excited torsional states. The latter is usually the vibrational modes of lowest frequency and is relatively well populated.

The theoretical methods to be applied to single top molecules have been reviewed by Lin and Swalen. ¹⁰⁰ In most cases the problem consists of a symmetric top attached to an asymmetric frame. ^{52,70} Extensions have been made to treat two-top molecules, ¹¹⁸⁻¹²⁰ asymmetric top and frame, ^{39,136} cis-gauche-trans configurations of C-C bonds, ^{122,123,147} and symmetric top molecules through excited states ^{87,88} and Coriolis effects. ¹⁴⁰

Herschbach¹³⁴ has listed the barrier values determined through 1962 in a complete review of experimental results.

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Section IX. INVERSION

Early microwave studies of ammonia^{8-12, 14-17} led to an immediate interest in the inversion problem. A number of twofold, potential functions^{2-6, 13, 21, 52, 53} were applied to ammonia to calculate the barrier height and inversion splittings. These functions have also been adapted to inversion in asymmetric rotors. ^{20, 47, 56, 58, 62} Recent interest has been directed toward near-planar molecules, ^{40, 44, 50, 61} and has led to the development of matrix elements in both the harmonic oscillator and quartic oscillator representations. ^{54, 55} These efforts have been aided by far-infrared vibrational data. ⁴³

The J-dependence of the inversion doubling has been treated with expressions of linear^{20, 47, 59} and exponential dependence. ^{18, 59}
Interactions with other molecular vibrations have been of considerable interest in ammonia^{29, 53} and methylamine. ^{24, 34, 35} The possibility of two coupled inversion-type motions was encountered in hydrazine. ^{47, 57}

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- 1. H.A.KRAMERS, Z.PHYSIK 39,828-840(1926) WAVE MECHANICS AND SEMI-NUMERICAL QUANTIZATION
- 2. M.BORN AND J.R.OPPENHEIMER, ANN.PHYSIK 4-84,457-484(1927) QUANTUM THEORY OF MOLECULES
- 3. B.PODOLSKY, PHYS.REV. 32.812-816(1928) QUANTUM-MECHANICALLY CORRECT FORM OF HAMILTONIAN FUNCTION FOR CONSERVATIVE SYSTEMS
- 4. P.M.MORSE, PHYS.REV.34,57-64(1929) DIATOMIC MOLECULES ACCORDING TO THE WAVE MECHANICS II. VIBRATIONAL LEVELS
- 5. C.ECKART.REV.MOD.PHYS.2.305-380(1930) THE APPLICATION OF GROUP THEORY TO THE QUANTUM DYNAMICS OF MONATOMIC SYSTEMS
- 6. R.S.MULLIKEN, REVS.MOD.PHYS.2,60-115(1930) THE INTERPRETATION OF BAND SPECTRA PARTS I, IIA, IIB
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1

THE MICROWAVE SPECTRUM OF REO3F

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- 594. V.F. VOLKOV, N. N. VYSHINSKII, AND N. K. RUDNEVSKII, IZV. AKAD. NAUK SSSR, SER. FIZ. 26, 1282-1285(1962) VIBRATIONAL AND ROTATIONAL SPECTRA OF TRIMETHYLCHLOROSILANE, TRIETHYLCHLOROSILANE, AND TRIETHYLCHLOROSTANNANE
- 595. W.ZEIL, W. HUETTNER, AND W. PLEIN, Z. NATURFORSCH 17A, 823-824(1962)
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- 597. S.S.BUTCHER, J.CHEM.PHYS.38, 2010-2311(1963) MICROWAVE SPECTRUM OF PROPYLENE SULFIDE
- 598. J.C.CHAUFFOUREAUX, ANN. SOC. SCI. BRUXELLES 77,171-176(1963) GROUND STATE OF VINYLIDENE FLUORIDE. DATA ON THE FIRST EXCITED STATE
- 599. A.P.COX AND A.S.ESBITT, J.CHEM.PHYS.38, 1636-1643(1963) FUNDAMENTAL VIBRATIONAL FREQUENCIES IN KETENE AND THE DEUTEROKETENES
- 600. R.F.CURL, JR., V.M.RAO, K.V.L.N.SASTRY, AND J.A.HODGESON, J.CHEM.PHYS. 39,3335-3340(1963) MICROWAVE SPECTRUM OF METHYL ISOCYANATE
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- 602. L.ESTEROWITZ, J. CHEM. PHYS. 39, 247-248 (1963) ROTATIONAL TRANSITIONS AND CENTRIFUGAL DISTORTION IN THE UHF SPECTRUM OF FORMALDEHYDE

- 603. C.FLANAGAN AND L.PIFRCE.J.CHEM.PHYS.38.2983-2969(1963) MICROWAVE SPECTRUM .STRUCTURE.AND QUADRUPOLE COUPLING TENSOR OF ETHYL BROMIDE
- 604. R.E.GOEDERTIER J.FHYS.(PARIS)24,433-637(1963) ROTATION SPECTRA, QUADRUPOLE COUPLING, AND STRUCTURE OF VINYL BROMIDE
- 605. L.M.IMANGV AND A.A.ABDURAKHM4NOV,IZV.AKAD.NAUK AZERB.SSR SER. FIZ.-MAT. I TEKHN.NAUK 1963,79-82(1963) MICROWA 5 DECTRUM OF CD3CH2OH
- 606. L.M.IMANOV AND CH.O.KADZHAR, OPTIKA I SPEKTROSKOPIYA 14,300-301(1963) THE SUPERHIGH-FREQUENCY SPECTRUM AND DIPOLE MOMENT OF THE ETHANOL MOLECULE
- 607. R.KEWLEY, K.V.L.N. SASTRY, AND M. WINNEWISSER, J. MOL. SPECTRY. 10,418-441 (1963) THE MILLIMETER WAVE SPECTRA OF ISOCYANIC AND ISOTHIOCYANIC ACIDS
- 608. R.KEWLEY, K.V.L.N.SASTRY, M.WINNEWISSER, AND W.GORDY, J.CHEM.PHYS.39, 2856-2860(1963) MILLIMETER WAVE SPECTROSCOPY OF UNSTABLE MOLECULAR SPECIES I.CARBON MONOSULFIDE
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- 610. R.L.KUCZKOWSKI, J.AM. CHEM. SOC. 85, 3047-3048(1963) SULFUR MONOFLUORIDE-MICROWAVE SPECTRUM OF A SECOND ISOMER
- 611. R.L.KUCZKOWSKI AND E.B.WILSON, JR., J.CHEM.PHYS.39, 1030-1034(1963)
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- 612. R.L.KUCZKOWSKI AND E.B.WILSON, JR., J.AM. CHEM. SOC. 85, 2028-2029 (1963) MICROWAVE AND MASS SPECTRA OF SULFUR MONOFLUORIDE
- 613. V.W.LAURIE AND D.T.PENCE, J.CHEM.P' (38, 2693-2697(1963) MICROWAVE SPECTRA AND STRUCTURES OF DIFLUORGE SYLENES
- 614. I.N.LEVINE, J. CHEM. PHYS. 38, 2326-2328 (1963) STRUCTURE OF FORMALDOXIME
- 615. D.R.LIDE.JR., J.CHEM.PHYS.38,456-460(1963) MICROWAVE SPECTRUM AND STRUCTURE OF DIFLUOROAMINE
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- 617. J.S.MUENTER AND V.W.LAURIE, J.CHEM.PHYS.39, 1181-1182(1963) MICROWAVE SPECTRUM, STRUCTURE, AND DIPOLE MOMENT OF SILYL ACETYLENE
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- 620. I.A.MUKHTAROV, DOKL. AKAD. NAUK SSSR 151, 1076-1078(1963) MICROWAVE SPECTRUM OF THE F2HC-CH2F MOLECULE
- 621. I.A.MUKHTAROV, FIZ. PROBL. SPEKTROSKOPII, AKAD. NAUK SSSR, MATERIALY

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- 623. E.W.NEUVAR AND A.W.JACHE, J.CHEM.PHYS.39,596-599(1963) MICROWAVE SPECTRUM AND STRUCTURE OF PENTAFLUOROSULFUR BROMIDE
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- 625. T.N.SARACHMAN, J.CHEM.PHYS.39,469-473(1963) MICROWAVE SPECTRIM OF NORMAL PROPYL CHLORIDE
- 626. L.H.SCHARPEN AND V.W.LAURIE.J.CHEM.PHYS.39.1732-1733(1963)
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- 629. K.TAKAGI AND T.OKA, J.PHYS.SOC. JAPAN 18,1174-1180(1963) MILLIMETER WAVE SPECTRUM OF FORMALDEHYDE
- 630. K.TAKAGI AND S.SAITO, J. PHYS.SOC. JAPAN 18, 1840(1963) MILLIMETER WAVE SPECTRUM OF SO2
- 631. J.K.TYLER.J.MOL.SPECTRY.11.39-46(1963) MICROWAVE SPECTRUM OF NITRAMIDE
- 632. J.K.TYLER AND J.SHERIDAN, TRANS. FARADAY SOC. 59, 2661-2670 (1963) STRUCTURAL STUDIES OF LINEAR MOLECULES BY MICROWAVE SPECTROSCOPY
- 633. R.VAN RIET, ANN.SOC.SCI.BRUXELLES 77,18-29(1963) ROTATIONAL SPECTRUM OF THE S(34)02 MOLECULE IN THE FIRST VIBRATIONAL EXCITED STATE (12,800-30,000 MC.) AND COMPLIMENTARY STUDY OF THE S(32)02 AND S(33)02 MOLECULES IN THE RANGE 25,000-27,500 MC.
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- 637. A.BAUER AND J.BELLET.J.PHYS. (PARIS) 25.805-808(1964) ROTATION SPECTRA OF SOZ IN THE MILLIMETER REGION
- 638. A.BAUER AND J.BELLET, COMPT.REND.258,873-876(1964) ROTATION SPECTRUM OF SOZ IN MILLIMETER WAVELENGTHS(6 MM. AND 2.2 MM.)

- 639. R.A.BEAUDET, J. CHEM. PHYS. 40, 2705-2715(1964) MICROWAVE SPECTRUM, BARRIER TO INTERNAL ROTATION, AND QUADRUPOLE COUPLING CONSTANTS OF CIS-1-CHLOROPROPYLENE
- 640. S.S.BUTCHER AND E.B.WILSON, JR., J.CHEM. PHYS. 40, 1671-1677(1964)
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- 648. G.JONES AND W.GORDY, PHYS.REV.136,1229-1232(1964) SUBMILLIMETER-WAVE SPECTRA OF HCL AND HBR
- 649. R.KEWLEY, K.V.L.N.SASTRY, AND M.WINNEWISSER, J.MOL.SPECTRY. 12,387-401 (1964) MICROWAVE AND MILLIMETER WAVE SPECTRA OF HYDRAZOIC ACID
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- 654. J.MARTINS AND E.B.WILSON, JR., J.CHEM. PHYS. 41,570-571(1964)
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- 661. V.M.RAO AND R.F.CURL, JR., J.CHEM.PHYS.40, 3688-3690(1964)
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- 662. J.S.RIGDEN AND S.S.BUTCHER, J.CHEM.PHYS.40, 2109-2114(1964)
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